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*W. J. J. J.*

TRANSLATION

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(54) Name of the Invention: Alkaline Battery

(21) Application Number: 55-31379

(22) Filing Date: March 13, 1980

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## SPECIFICATION

1. Title of the Invention: Alkaline Battery

5 2. Scope of the Patent's Claims:

1. An alkaline battery, characterized in that expansion graphite is used as a conductive agent in a compound anode.

10

3. Detailed Explanation of the Invention

This invention relates to an improved type of an alkaline battery. The purpose of this invention is to provide an alkaline battery which has excellent discharge characteristics and at the same time is easy to manufacture.

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When caustic potash or a similar aqueous solution characterized by a high boiling temperature is used as a battery electrolyte, manganese dioxide, silver monoxide, silver dioxide, hydrogen oxide, nickel oxide, or a similar oxide is often used for the active substance of the anode, while amalgamation zinc is used for the active substance of the cathode. However, a very urgent objective presently is that the discharge characteristics of these active substances need to be improved.

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The key point being that the discharge characteristics of the substances presently used need to be improved to enable their efficient utilization, said objective — seen from this perspective — also relates to the efficient utilization of active substances used in conductive agents.

25

Incidentally, although the crystalline graphite or acetylene black form of conductive agents is presently used, both of these agents are characterized by specific deficiencies, and thus it could not be said that their performance is satisfactory. In other words, while crystalline graphite per se is characterized by a low electric resistance, because the

contact resistance between the particles is high, the internal resistance of the anode composite is not low enough. On the other hand, although the resistance between the particles of acetylene black is low thanks to its structure, the formation characteristics of acetylene black are extremely poor, which is a defect preventing its efficient use in battery electrolytes. Furthermore, these problems will not be solved if the crystalline graphite is used jointly with acetylene black.

In view of the above described problems, this invention provides an alkaline battery which enables excellent discharge characteristics and is easy to manufacture, by using a conductive agent in the anode substance for which expansion graphite is used in an alkaline battery.

For the expansion graphite used as a conductive agent in accordance with this invention it is possible to use graphite containing expanded surface layers in the carbon lattice, for instance by using a smoke generating nitric acid with graphite, or concentrated sulfuric acid and concentrated acetic acid, chromic acid and concentrated sulfuric acid, perchloric acid, chromic acid and phosphoric acid, or a similar oxidizing agent can be applied during an oxidation treatment in order to generate a compound structure between the surface layers of the carbon lattice of the graphite. This can be followed by washing with water, or the product can be heated as is to at least 100°C, for instance by subjecting it to heat until a temperature of 350°C is reached, causing the compound formed between the layers of the graphite to gasify.

Also, because this expansion graphite displays intermediate characteristics with acetylene black and graphite, it has not only extremely good compressibility characteristics, but is also characterized by a much lower electric resistance than crystalline graphite. In addition, because it also absorbs electrolyte well when such a product is used as conductive agent, an anode compound can be formed easily from this product in order to improve the discharge characteristics.

It is possible to utilize only a small amount of expansion graphite that should be used for the conductive agent as compared to the amount of crystalline graphite that was used according to prior art. In a common type of an active anode substance it is possible to use approximately 5 ~ 20 parts by weight of this agent per 100 parts by weight of the active anode substance (the terms parts will be used hereinafter in this meaning). In addition, it is also possible to use a conductive agent which has a small amount of crystalline graphite added to the expansion graphite.

An exemplary embodiment of an alkali manganese battery LR according to the invention is explained hereafter.

Table 1 shows how an anode compound that was molded to cylinder shape by applying molding pressure to an anode compound in the form of a powder at 2 t/cm<sup>2</sup>. Table 1 shows the number of defective items per 1,000 items of anode compound formed in this manner.

As evident from Table 1, anode can (2) was filled with anode compound (1) obtained in this manner, which was introduced into a separator (3) having the shape of a cup made of vinylon rayon paper or vinylon paper, etc., was curled inside the opening [illegible] of anode (2). After impregnation with electrolyte, the compound was mixed with carboxymethyl cellulose, polyacrylic acid, or a similar electrolytic solution in order to create a gel, which was dispersed in amalgamation zinc to create [illegible, probably cathode] agent (4), and the internal part of separator (3) was filled with it. Gasket 8, containing rubber ring (5) as well as cathode collecting rod (6) and cathode terminal plate (7) inserted in the gasket was placed on top of anode can (2); after attachment of anode terminal plate (9) and annular insulation plate (10) the outer part of can (12) was caulked with resin tube (11) and sealed, creating the inner structure of a sealed manganese alkaline battery.

The amount of composite powder used to form the composite anode is shown in Table 1, along with the amount of electrolyte injected in the anode composite and the resulting discharge times measured when performing continuous discharges of said manganese alkaline battery at 20°C and 10 Ω. In addition, the electrolyte used in this case was an aqueous solution of caustic potash containing 5.2 weight % of zinc oxide dissolved in 35 weight % of caustic potash.

As follows from Table 1, when battery A, in which expansion graphite was used as a conductive agent, was compared to a conventional battery type B using the crystalline form of graphite, fewer defects occurred in forming the anode composite, the amount of electrolyte absorption by the anode compound was higher, and also the discharge performance was excellent.

Moreover, this invention is not limited only to the present example of a manganese alkaline battery, it can be applied with optimal results also to other types of alkaline batteries, such as a mercury, silver oxide, silver dioxide or nickel batteries, etc.

#### 4. Brief Explanation of Figure

Figure 1 shows a sectional view of an exemplary embodiment of a simple manganese alkaline battery according to this invention.

(1) ... anode composite agent

Patent Applicant: Hitachi-Maxell K.K. Company

Representative: Akira Miwa, Patent Attorney

Table 1

S T R U C T U R E	Battery	A	B
	Manganese dioxide (parts)	180	180
	Expansion graphite (parts)	30	-
	Crystalline graphite (parts)	-	33
Amount of composite powder used to form the anode composite (g)		7.5	7.6
Number of defects per 1,000 items of anode composite agent		1	23
Amount of electrolyte injected in the anode composite (g)		1.8	1.5
Continuous discharge time at 10 $\Omega$ (h)		14	12



1995年 7月 10日

株式会社黒鉛工業所

特殊処理黒鉛 BSP シリーズを使用するにあたって

1. アルカリ乾電池高性能用として使用する場合

(1) 黒鉛の添加量

アルカリ電池正極における二酸化マンガ ( $MnO_2$ ) と、黒鉛 (G) の混合割合について

4～5年前迄	$MnO_2$ : G = 9 : 1	( G の添加量 9 % )
現在の主流	$MnO_2$ : G = 13 : 1	( " 7.1 % )
高性能タイプ	$MnO_2$ : G = 20 : 1	( " 4.8 % )

電池を高性能化 (放電容量を大きくする) する為には、 $MnO_2$  の量を多くすれば良い。

BSP シリーズは、現在使用されている一般の天然又は、人造黒鉛に比べ電気抵抗が低く、かつ成形状が良好である。

その結果、電池内で黒鉛の添加量を減らし、 $MnO_2$  の添加量を増やす事が出来た。

(2) 混合について

BSP は、従来の黒鉛に比べて高密度が小さいため、 $MnO_2$  等との混合が難しい。

日本の電池メーカーでのテスト状況からも、 $MnO_2$  との混合のしにくさが指摘されている。このため、BSP を均一混合するためには、混合力が強い混合機を使用する必要がある。

BSP の混合に適する混合機としては、別紙のハイスピードミキサーが推奨出来る。このミキサーは、電池製造用に限らず、BSP の混合において敎社で実績があり、好結果を得ている。

2. リチウム一次電池に使用する場合

BSP をリチウム一次電池に使用する目的は、 $MnO_2$  と BSP を混合した合材をペレットに成形する際のバインダー効果であるが、この場合もアルカリ電池と同じく混合がポイントである。特にバインダー効果を得るためには、出来るだけ黒鉛の粒子を壊さないようにかつ、均一混合する必要がある。その点でも上記のハイスピードミキサーは、非常に短時間で均一混合できるので、BSP の特性を壊さないで混合可能である。

以 上

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表1 特殊処理黒鉛と鱗片状黒鉛の粉体特性

	特殊処理黒鉛 BSP-40AS	鱗片状黒鉛 BP-40A
固定炭素 (%)	98.59	99.50
灰 分 (%)	0.39	0.11
揮発分 (%)	1.02	0.39
水 分 (%)	0.40	0.20
比表面積 ( $\text{m}^2/\text{g}$ )	25.3	3.9
かさ密度 ( $\text{g}/\text{cm}^3$ )	0.085	0.235
粒度分布 ( $\mu\text{m}$ )		
$D_{10}$	10.24	11.02
$D_{50}$	40.06	41.66
$D_{90}$	89.33	90.75

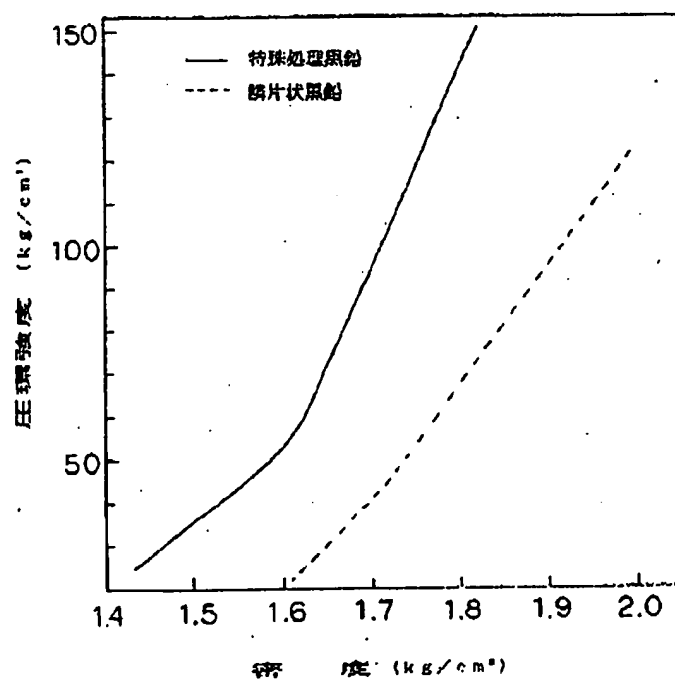


図1 黒鉛の圧環強度

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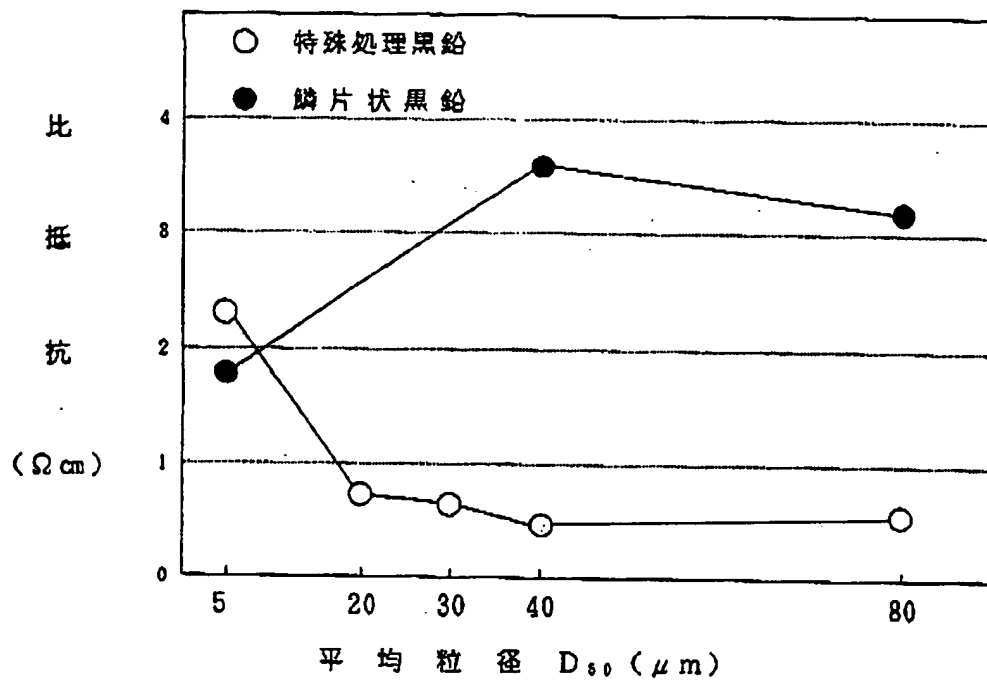


図 2,  $\text{MnO}_2 - \text{C}$  合材の比抵抗

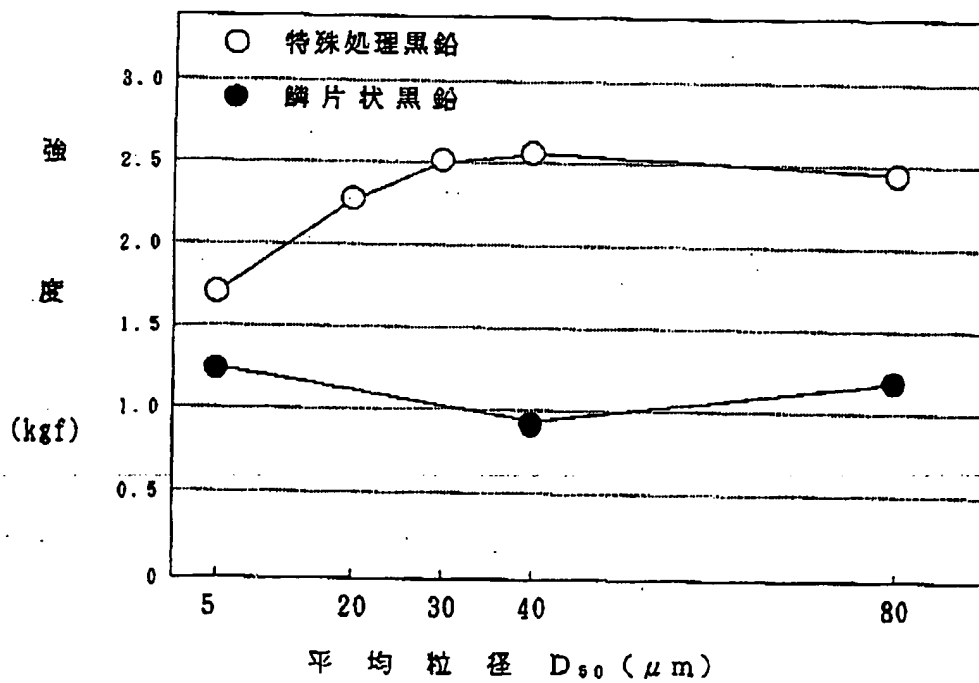


図 3,  $\text{MnO}_2 - \text{C}$  合材の成形強度

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平成7年5月22日

## 特殊処理黒鉛BSPについて

(株)中越黒鉛工業所

### 1. はじめに

コイン型リチウム一次電池の正極は、一般に活物質である二酸化マンガンを導電材としてアセチレンブラック、黒鉛等のカーボン材を混合し、成形体の強度を高める為にバインダーを用いている。このため、成形体の乾燥による生産性の低下及び成形体の導電性の低下が生じている。今回、このカーボン材として膨張黒鉛を原料とする特殊処理黒鉛BSPを使用し、バインダー量の低減、究極にはノーバインダーを目的に正極合材の成形テストを行ったので報告する。

### 2. 特殊処理黒鉛の製法

特殊処理黒鉛は膨張黒鉛を原料として製造する。膨張黒鉛は天然産鱗片状黒鉛を濃硫酸と強酸化剤である濃硝酸、過酸化水素、過塩素酸塩、過マンガン酸塩などで処理し、黒鉛層間化合物を生成した後、水洗、乾燥して製造する。膨張黒鉛を950～1100℃の高温下で、急激に加熱すると、黒鉛の層間に挿入されている硫酸や硫酸イオンが気化し、黒鉛内部において気化による圧力が発生し、瞬時に黒鉛の層間を100～300倍に押し広げる。これを特殊な方法によって粉砕したものが特殊処理黒鉛BSPである。

### 3. 特殊処理黒鉛の特性

#### 3-1. 粉体特性

表1に同一粒径の特殊処理黒鉛と鱗片状黒鉛の特性比較をしめす。特殊処理黒鉛は、鱗片状黒鉛に比べ、比表面積が非常に大きく、かさ密度が小さい。写真1、2にそれぞれのSEM写真を示すが、特殊処理黒鉛は、粒子表面にハニカム構造を有し、かつ薄肉化していることがわかる。

図1に黒鉛単体で成形した時の成形体強度の一例を圧壊強度として示すが、特殊処理黒鉛は鱗片状黒鉛に比べ著しく高強度を示す。

#### 3-2. 二酸化マンガ合材特性

導電材として、鱗片状黒鉛と特殊処理黒鉛を用い、市販の二酸化マンガとバインダーを添加せずに混合し、合材を作製した。合材の混合比は、重量比で二酸化マンガ：カーボン材=100：7とした。この二種の合材を電気抵抗及びペレット強度について比較した。

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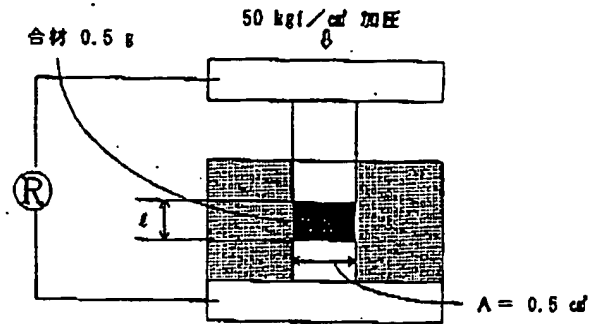


#### (1) 電気抵抗

合金0.5gを内径0.8cmの型に入れ  
圧力50kgf/cm<sup>2</sup>で加圧しながら0.1Aの  
電流を流し抵抗を測定し、①式より  
比抵抗を求めた。

$$\rho = R \cdot A / l \quad (\Omega \text{ cm}) \quad \text{--- ①}$$

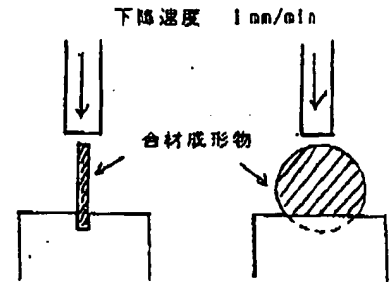
結果を図2に示すが、黒鉛の平均  
粒径5 $\mu\text{m}$ では黒鉛の種類によって  
比抵抗に顕著な差はみられないが、  
20 $\mu\text{m}$ 以上の領域では、特殊処理黒  
鉛の方が大幅に低抵抗と成っている。



#### (2) ペレット強度

合金1gを内径15mmの金型におい  
て荷重8tで2回加圧成形してペレ  
ットを作製した。これを右図の要領  
で破壊強度を測定した。

結果を図3に示すが黒鉛の粒径を  
問わず特殊処理黒鉛を使用したもの  
が、強度が高い。また特殊処理黒鉛  
を使用した合金の強度は平均粒径40  
 $\mu\text{m}$ で極大となっている。



#### 4. まとめ

特殊処理黒鉛を使用した二硫化マンガン合金は、鱗片状黒鉛を使用した合金に比べ電気抵抗が低く、ペレットの強度も高くなる事が分かった。またその時の特殊処理黒鉛の平均粒径は、40 $\mu\text{m}$ が最適であることが明らかになった。

特殊処理黒鉛を使用する事によって合金の電気抵抗が低くなる原因は、特殊処理黒鉛の比表面積が大きいこと、黒鉛同士の接触する面積が、通常の黒鉛に比べ大きく成っているためではないかと考えられる。また、合金の強度が高くなるのは、ハニカム構造を持つ特殊処理黒鉛粒子同士がからみ合うように結合をしているためであると考えられる。

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JUN. 20, 1966

CHIYETSU GRAPHITE WORKS CO., LTD.

CHARACTERISTICS OF GRAPHITE FOR ALKALINE BATTERY

			CA-6A/11G1	CA-7D/11G1	CA-R	KS-15	DSP-10AS /11G1
Industrial analysis	Fixed Carbon	(%)	99.39	99.38	99.23	99.26	98.95
	Ash	(%)	0.11	0.13	0.22	0.04	0.14
	Volatile Matter	(%)	0.50	0.49	0.55	0.70	0.91
	Moisture	(%)	0.40	0.30	0.10	0.10	0.40
Bulk Specific Gravity (g/cm <sup>3</sup> )			0.117	0.160	—	0.205	0.079
Specific Surface Area (m <sup>2</sup> /g)			10.7	22.5	—	12.5	28.4
Particle Size	D <sub>10</sub>	(μm)	2.88	2.96	—	3.19	3.98
	D <sub>50</sub>	(μm)	6.17	6.66	—	7.92	9.96
	D <sub>90</sub>	(μm)	12.35	14.54	—	16.06	22.84
	MV	(μm)	7.09	8.03	—	8.98	12.10
Impurities Quantitative Analysis	Fe	(ppm)	25	24	75	50	108
	Mo	(ppm)	< 1	< 1	< 1	< 0.5	< 1
	V	(ppm)	< 5	< 5	< 5	4	< 5
	Cr	(ppm)	< 5	< 5	< 1	1	11
	Cu	(ppm)	< 1	< 1	< 1	2	< 1

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